Talanta 206 (2020) 120214

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A solvatochromic AIE tetrahydro[5]helicene derivative as fluorescent probes for water in organic solvents and highly sensitive sensors for glyceryl monostearate

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ARTICLE INFO

Keywords:
Tetrahydro[5]helicene
Solvatochromism
Twisted intramolecular charge transfer
Aggregation-induced emission
Glyceryl monostearate

ABSTRACT

In this paper, a tetrahydro[5]helicene-based imide dye with thienyl group (THID) was studied on its solvatochromism and aggregation-induced emission (AIE) properties by dissolved in various organic solvents. The linear relationship between Stokes shift and aprotic solvent polarity parameter was well fitted with Lippert-Mataga model. Furthermore, Stokes shift also were positively correlated with the normalized molar electronic transition energy, suggested that THID exceptionally depends on solvent polarity for twisted intramolecular charge transfer. In addition, THID demonstrated typical AIE features when adding large amounts of water into good solvent. Meanwhile, it can function as intensity and wavelength-based fluorescence sensor for detecting low-level water content in water soluble solvents, even the low of detection was 0.014 vol% in ACN. Therefore, a simple and highly selective fluorescence analysis for glyceryl monostearate has been established on basis of its AIE property.

1. Introduction

Fluorescent organic dyes have attracted extensive attentions in recent years due to their widely potential applications in organic light emitting diode [1], luminescence sensors [2,3], biological imaging [4,5], and so on. In general, the main drawback of traditional organic fluorescence dyes, suffered from the aggregation-caused quenching (ACQ) effect, can show only outstanding luminescence in diluted solution yet nearly non-fluorescent in solid state [6,7]. However, developing new organic photo-active compounds with high fluorescence efficiency in solid-state is very attractive and important, owing to their extensively practical applications in liquid crystals [8,9], optoelectronic materials [10,11], organic solid-state lasers [12] and other areas.

Aggregation-induced emission (AIE) is a photophysical phenomenon, which is contrary to the ACQ. Since Tang's group first reported the AIE-active dyes [13,14], numerous molecules with AIE properties have been developed and have been widely applied in optoelectronic materials and sensors. Recently, some special molecules, which could exhibit both twisted intramolecular charge transfer (TICT) and AIE properties, have attracted extensive attentions, because of their dual fluorescence-response to solvent polarity and luminophones aggregation [15–17]. When fluorescent molecules exhibited both TICT and AIE processes, TICT could cause solvatochromism of dyes in different organic solvents and AIE was primarily involved in manipulating their emission intensity in aggregation even in solid states, respectively. It is well know that TICT and AIE processes can be affected by the compound structure. It was found that most of those dyes with TICT and AIE processes were "D-π-A" type compounds with twist structures [18]. Considering that new kinds of fluorescent helicene derivatives bear these two structural features, they might also exhibit TICT and AIE properties.

Recently, a class of polycyclic aromatic compounds with nonplanar helical skeletons synthesized by fused benzene or other aromatic rings, Tetrahydro[5]helicene-based imide dyes have been synthesized by Chen's group [19–22]. These compounds could emit intense fluorescence, not only in solution, but also in the solid state. These derivatives show large Stokes shifts and tunable fluorescent emission, through introducing donating unit into the helical skeleton. In addition, the density functional theory calculations demonstrated that the aromatic substituents have influence on the electron configuration of imide dyes, which could cause intramolecular charge transfer (ICT) [23,24]. Some of them combining twisted structure between aromatic substituents and imide units could show an interesting AIE when they were self-assembled into aggregations in the solid state and in solvents with poor

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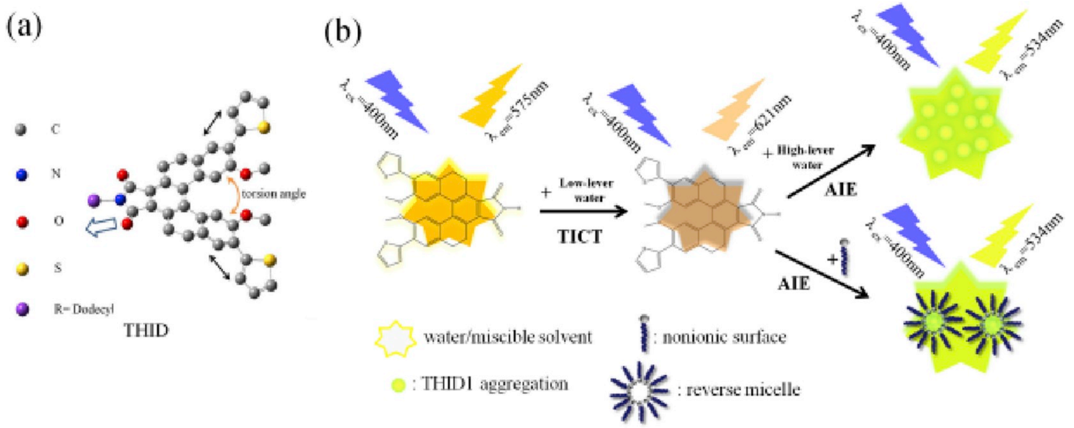
https://doi.org/10.1016/j.talanta.2019.120214
Received 9 May 2019; Received in revised form 19 July 2019; Accepted 31 July 2019



Scheme 1. (a) Packing mode of THID. (b) Schematic illustration of the process of fluorescence of THID were "turn off" by low-lever water and "turn on" by high-level water or GMS in water/miscible solvents.

solubilities, due to the restriction of intramolecular motion (RIM) mechanism [19]. However, reports of AIE helicene derivatives, especially those displaying AIE and TICT, were still quite rare. Therefore, developing and using helicene derivatives with AIE and TICT are very important in numerous fields.

Herein, a tetrahydro[5]helicene based imide dye with thienyl (THID), combing π conjugated helical skeleton, strong intramolecular push–pull electronic interaction between 2-thienyl and imide moiety with a twist dihedral angle (Scheme 1 a), could show intense and steady-going fluorescence in both solution and solid state [20]. Similar to most of "D-π-A" type dyes, the fluorescence of THID was strongly affected by the solvent polarity because of its TICT [25,26]. For these compounds, one of features is that a pronounced solvatochromism occur in their fluorescence with gradually changing the solvent polarity. Therefore, THID can serve as a super-sensitive fluorescent indicator for detecting low-level water in organic solvents. More interestingly, THID has also been employed as solvatochromic sensors for detecting water content in Tetrahydrofuran (THF) or dioxane (Diox), depending on changing the emission wavelength. In addition, THID showed distinguishing AIE features when the polarity of solvent medium was changed from general organic solvents to water. Therefore, on the basis of "cage effect" [27,28], a simple, shortly time-consuming, highly sensitive and selective AIE-active fluorescent sensor for detecting the glyceryl monostearate (GMS) has been established in this work (Scheme 1. b). Glyceryl monostearate, one of the most common nonionic surfactants, has attracted numerous attentions, which can be used as emulsifier, stabilizer, and dispersant, etc [29,30]. However, excess GMS are harmful to human's health. Due to its surfactant structure with hydrophilic hydroxyl groups, GMS could form reverse micelles with hydrophilic core in nonaqueous solutions. To our best knowledge, it is the first time to detect the GMS based fluorescence analysis with very low LOD, even up 3 orders of magnitude lower than that of reported chromatographic method [31].

2. Experimental

2.1. Materials

2-dodecyl-8,11-dimethoxy-7,12-di(thiophen-2-yl)-4,5,14,15-tetrahydro-1H-dinaphtho[2,1-e:1′,2′-g]isoindole-1,3(2H)-dione (THID) was synthesized by Chen's group in Institute of Chemistry Chinese Academy of Sciences. N, N-dimethylformamide (DMF) and acetonitrile (ACN) of chromatographic-reagent grade (≥99.9%), Tetrahydrofuran (THF) and dioxane (Diox) of spectral-reagent grade (≥99.5%) were purchased from Aladdin (Shanghai, China). Other organic solvents were analytical-reagent grade (≥99.5%), bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Distillation was used to purify THF, Diox and Acetone prior to the usage of these solvents. THF and Diox were distilled under nitrogen atmosphere from sodium and benzophenone. Acetone was heated at reflux over potassium permanganate ($KMnO_4$) and then pre-dried over calcium sulphate ($CaSO_4$) before distilling. All organic solvents were stored in a dry environment to avoid that the moisture was introduced. Other chemicals were of analytical grade and used without further purification. The ultra-pure water was manufactured by a Milli-Q water purification system (USA). In addition, sample cells were sealed in the detection processes.

2.2. Instrumentation

All fluorescence spectra and fluorescence lifetime decay curves were measured by a FS5 fluorescence spectrometer (Edinburgh Instruments, England), and absorption spectra were recorded by employing a UV-2600 UV–Vis spectrophotometer (Shimadzu, Japan). The experiments of dynamic light scattering (DLS) were performed by employing NanoBrook Omni Dynamic Light Scattering (DLS) Particle Sizer and zeta potential Analyzer (Brookhaven, America). The experiments of confocal laser fluorescence microscopy (CLFM) were conducted from Leica TCS SP8 Laser Scanning Confocal Microscopy (Leica, Germany). The pattern of nonionic surfactant vesicles were observed through a field emission scanning electron microscopy S48000 FESEM (Hitachi, Japan) and transmission electron microscopy H-7650 (Hitachi, Japan). The standard method was utilized to determine the fluorescence quantum yields (Φ_f) of the THID in different solvents using quinine sulphate in 0.05 M H_2SO_4 aqueous solution as a reference [32], applying the equation:

$$\varDelta\ f= \frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1}$$

where, F is the fluorescence integrated intensity, A is the absorption intensity, n is the refractive index, and the parameters with subscript (s) are something about quinine.

3. Results and discussion

3.1. Solvatochromism

The thienyl group was introduced into tetrahydro[5]helicene skeleton with imide unit to form the D-π-A conjugation, thereby the photophysics property of this compound should depend on the solvent polarity in solution. Therefore, the absorption and fluorescence spectra of THID in a series of frequently used solvents with different polarities were detailedly investigated in this work, and the obtained data were summarized in Table S1. Fig. 1a shows the absorption fluorescence

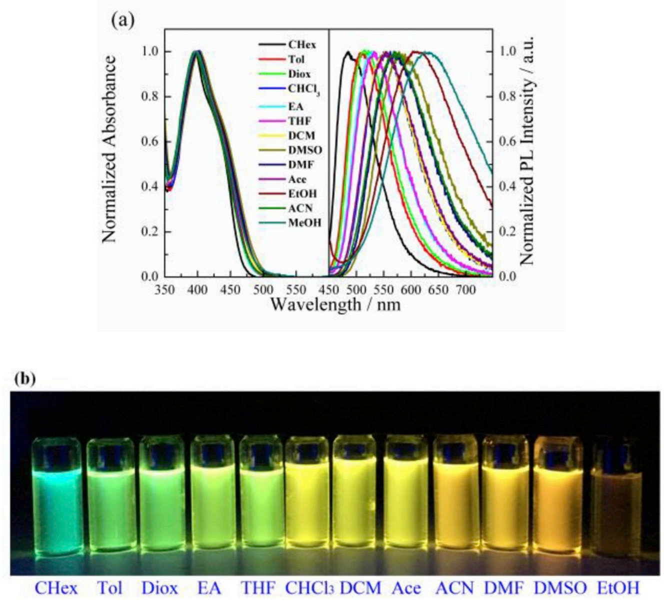


Fig. 1. (a) Normalized absorption (left) and fluorescence emission spectra (right) of THID in various solvents. (b) Photographs of THID in various solvents taken under UV light (365 nm). Concentration: 1 μM.

spectra of this compound in the various solvents. The maximum absorption wavelength was found to locate at ca. 400 nm, likely caused by the $\pi-\pi^*$ transition absorption of the big conjugate system, with very slight shift of only a few nanometers when the solvent polarity was increased from apolar (cyclohexane) to highly polar (methanol). Therefore, it was somewhat surprising to that the fluorescence spectra of THID exhibited a very pronounced bathochromic-shift (from 493 nm to 625 nm) as opposed to the absorption, and correspondingly, the luminescent light of corresponding solutions was changed from green to orange under UV irradiation. These results indicated that the emission properties of this dye were strongly dependent-solvent. This result could be likely attributed to the combination of the electron-donating thienyl unit and the electron-accepting imide group resulting in that, along with twisted D-π-A structure, TICT processes in THID molecule could be facilitated to produce prominent solvatochromic fluorescent property.

The solvatochromic property on fluorescence emission of compound THID was further investigated by following the Lippert-Mataga model, in which the Stokes shift ($\Delta\nu$) was related to solvent polarity parameter (Δf) in thirteen solvents with a wide range of polarity (Fig. 2a). It was found that, a great linear correlation between $\Delta\nu$ and Δf, with a large slope of 8068 cm^{-1} could be obtained when protic solvents (ethanol and methanol) were excluded, indicative of the excellent solvent-polarity dependence of this compound. Furthermore, the solvatochromism can be indicated by the good linear relation between $\Delta\nu$ and the normalized molar electronic transition energy (E_T^N) of the dye (Fig. 2b) [33,34]. These results supported that, the THID molecule was strongly dependent-solvent-polarity leading to solvatochromism. All of these results also revealed that there was a large variation of the dipole moment between the TICT excited state and the ground state due to charge redistribution. The fluorescence quantum yield and fluorescence lifetime (τ_{ave}) of THID dissolved in protic solvents showed obvious decrease. In particular, τ_{ave}, the excited state lifetime [35,36], was recorded with fast decay (Table S2). This suggested that THID molecules may form excited-state proton-transfer complexes with solvent molecules in protic solvents, of which acts between the carbonylic oxygen of solutes and the OH groups of solvents [37,38]. This also accounts for that the points of hydrogen bonding solvents are deviated from the linear regression range of the Lippert-Mataga model. Taken together, these results could reveal that THID seem to likely play as a suitable solvent polarity sensor.

Note: Δ f= $\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1}$, where $_\varepsilon$ is the static dielectric constant and n is the refractive index of the solvent. E_T^N is the normalized molar electronic transition energy. $\Delta\nu=\lambda_{\text{abs}}-\lambda_{em}$ in cm^{-1}.

3.2. Aggregation-induced emission

The solvatochromism of THID is generally associated with TICT mechanism, and the emission in the TICT state can be modulated by restricting intramolecular motion to be AIE-active in aqueous media [39]. To examine whether THID is AIE-active or not, its emission properties in organic solvent/water mixture was investigated. A series of common solvents, such as Diox, THF, DMF, Ace and ACN were systematically studied. The curves of maximum emission intensity and emission wavelength related to water content (f_w, water fraction) were showed respectively in Fig. 3 and photographs of the THID in DMF with different f_w taken under UV irradiation were shown in Fig. 3 inset. The emission intensity of THID was largely quenched until f_w = 30 vol% and a new strong-emitted fluorescent peak appears at f_w = 40 vol% with unusual blue shift, from 621 nm to 534 nm. Whereafter, increasing in the f_w > 40 vol%, no shift of the emission peak could be observed. The unusual blue shift of ca. 87 nm was indicative of the strong intermolecular self-aggregate behavior, resulting in the restricted intramolecular rotations. The maximum emission of THID aggregation at

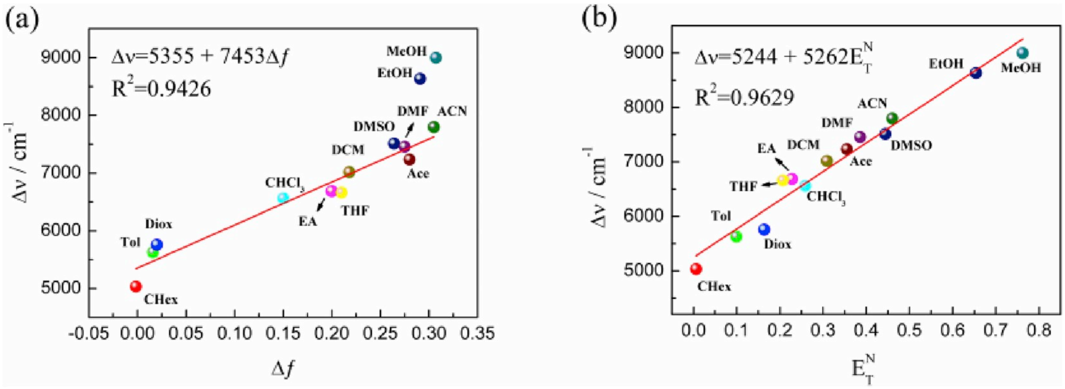


Fig. 2. (a) Stokes shifts ($\Delta\nu$) of compound THID versus Δf and points of EtOH and MeOH were excluded from the fit. (b) Stokes shifts ($\Delta\nu$) of compound THID versus E_T^N.

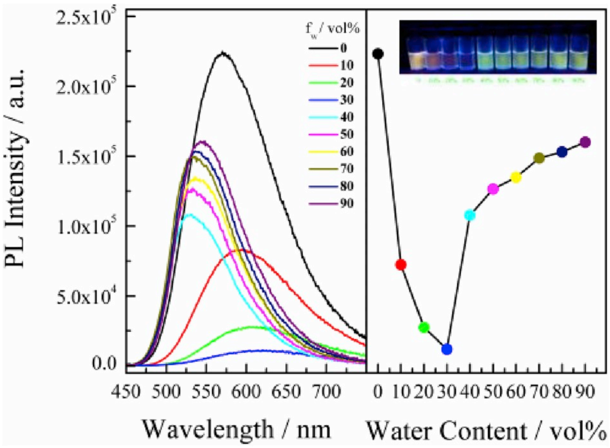


Fig. 3. Fluorescence emission spectra (left) and plots of emission intensity (right) of THID in the presence of different f_w (0–90 vol%) in DMF solution. Inset: photographs of THID in the DMF/water mixture taken under UV light (365 nm).

534 nm was almost in agreement with that in its solid state (Fig. S1). The UV–vis absorption of THID in the DMF/water mixture further indicated the formation of aggregation (Fig. S2). In addition, dynamic light scattering (DLS) was employed to probe the formation of aggregates in mixed solutions (Fig. S3). The average hydrodynamic size mainly located at (100.24 ± 8.01) nm in DMF/water mixture with 80% water content. The scanning electron microscopy (SEM) images also supported the formation of aggregations, seemly aggregations formed in DMF/water mixture (2:8, v/v) (Fig. S4). Therefore, the THID compound could be considered to be AIE-active. This seemed to result from two aspects: (i) restricted intramolecular rotations could be caused by impeding relative motion between thienyl and helical skeleton; (ii) this molecule was placed in nonpolar environment and partially could prevent the TICT state, endowing the aggregations with intense emission [15].

Introducing various amount of water which could facilitate this molecule to aggregate were not well agree in different solvents, for example, the fluorescence intensities abruptly increased when the f_w were 60 vol% and 40 vol% for THF and DMF, respectively (Fig. S5). This result is dependent on distinguishing solubility, the compound THID could be considered to be much easier dissolvable in volatile THF. Therefore, much more poor solvents should be introduced into the solution to induce aggregation. Consequently, water can be seen as an important affecting factor for the fluorescent properties of THID.

3.3. *THID was employed as an indicator for detecting low-level of f_w*

Above results indicated that the fluorescence of THID is dependent on solvent-polarity, thus THID can be employed as a fluorescent sensor for detecting water content in organic solvents. Therefore, the emission behavior of THID in some aprotic water/miscible solvents was investigated (Figs. S6–S10). After a certain volume of water was introduced into every tested organic solvent, the fluorescence intensity of THID generally underwent to decrease, accompanied with significantly red shift of the maximum emission peak. For example, in dioxane case, the emission intensity was found to be effectively quenched, accompanied with a large shift of maximum emission peak from 518 nm to 595 nm as the water content was increased from 0 to 30 vol%, and a good linear relationship ($R^2 = 0.9941$) of fluorescence intensity versus water fraction can be obtained when water content was smaller than 20 vol%. Moreover, similar linear relationship could be established in other water/miscible solvent systems, listed in Table 1. The limit of detection (LOD) could be estimated based on $3\delta/|k|$. The probe was found to be sensitive to water.

Table 1
Linearity range and LOD of THID for low-level water determination in various solvents.

Solvent	Linearity range (vol%)	Limit of detection (vol%)	R^2
Diox	0.15–20	0.050	0.9941
THF	0.11–10	0.036	0.9968
DMF	0.091–10	0.030	0.9918
Ace	0.20–5.0	0.065	0.9951
ACN	0.041–5,0	0.014	0.9914

More interestingly, from CIE coordinates corresponding to emission color of different f_w solvents (Fig. S11 and Table S3), marked significant color change was found when THID was dissolved in water/Diox or water/THF mixed solution, compared with other organic solvent systems. The emission wavelength of THID as a function of water content was found to have a good linear relationship as the water content was enhanced. A wide linear relationship of water contents from 0.31 vol% to 35 vol% with LOD of 0.10 vol% in dioxane and from 0.43 to 4.5 vol% with LOD of 0.16 vol% in THF, respectively, could be obtained (Fig. 4). Accordingly, the color of fluorescence was found to change from green to orange under the irradiation of a UV lamp. Therefore, these observations could reveal that THID can work as a suitable water indicator to detect low-level water content in several aprotic water/miscible solvents.

3.4. *THID was served as a probe for detecting GMS*

Considering that THID compound can exhibit both TICT and AIE characteristics in water/organic mixed solutions. It is interesting to develop a sensitive method to recognize surfactants in "turn-on" mode instead of adding large water, which could offer a "water cage" for THID molecule to aggregate.

Glyceryl monostearate is a water-in-oil nonionic surfactant with hydrophilic hydroxyl groups, which form reverse micelles with hydrophilic core in nonaqueous solutions. Considering that the AIE-active property of THID and the "cage effect" caused by surfactant, it should be a suitable probe for GMS in DMF/water mixture (7:3, v/v) with a fluorescence turn-on sensing mode. A blue shift of the maximum emission peak of THID and the significant fluorescence enhancement with increasing GMS concentration could be observed (Fig. 5). The obtained new maximum fluorescence emission at 534 nm was supportive of THID aggregations. The turn-on fluorescence can even be directly observed by naked eye under UV irradiation (Fig. 5 inset). A good linear relationship ($R^2 = 0.9991$) between GMS concentration (c_{GMS}) and I/I_0 could be achieved in range of 3.0–153 μg/mL, and the LOD was 0.99 μg/mL. As shown in Fig. S12 and Table S4, the fluorescence lifetime measurements were further carried out to understand the influence of GMS on THID. The average fluorescence lifetimes of THID probe was 0.976 ns, whereas longer τ_{ave} of 5.502 ns was found in the presence of GMS, suggested that THID aggregations could produce a longer τ_{ave}.

In general, critical micelle concentration (CMC) value of reverse micelle formed by nonionic surfactants should be lower than those of the normal micelles, since the weak dipole-dipole interactions [40]. The CMC value of GMS could be determined from the emission intensity ratio of $I_{621\ nm}/I_{540\ nm}$ plotted against the c_{GMS} [41] (Fig. 6a). The intersection of two tangent lines was indicative of the CMC value at 25 μg/mL. Form the SEM image of GMS in DMF/water mixture (7:3, v/v), the spherical reverse micelle could be observed (Fig. S13). Furthermore, the CLFM was utilized to observe reverse micelles adding dye

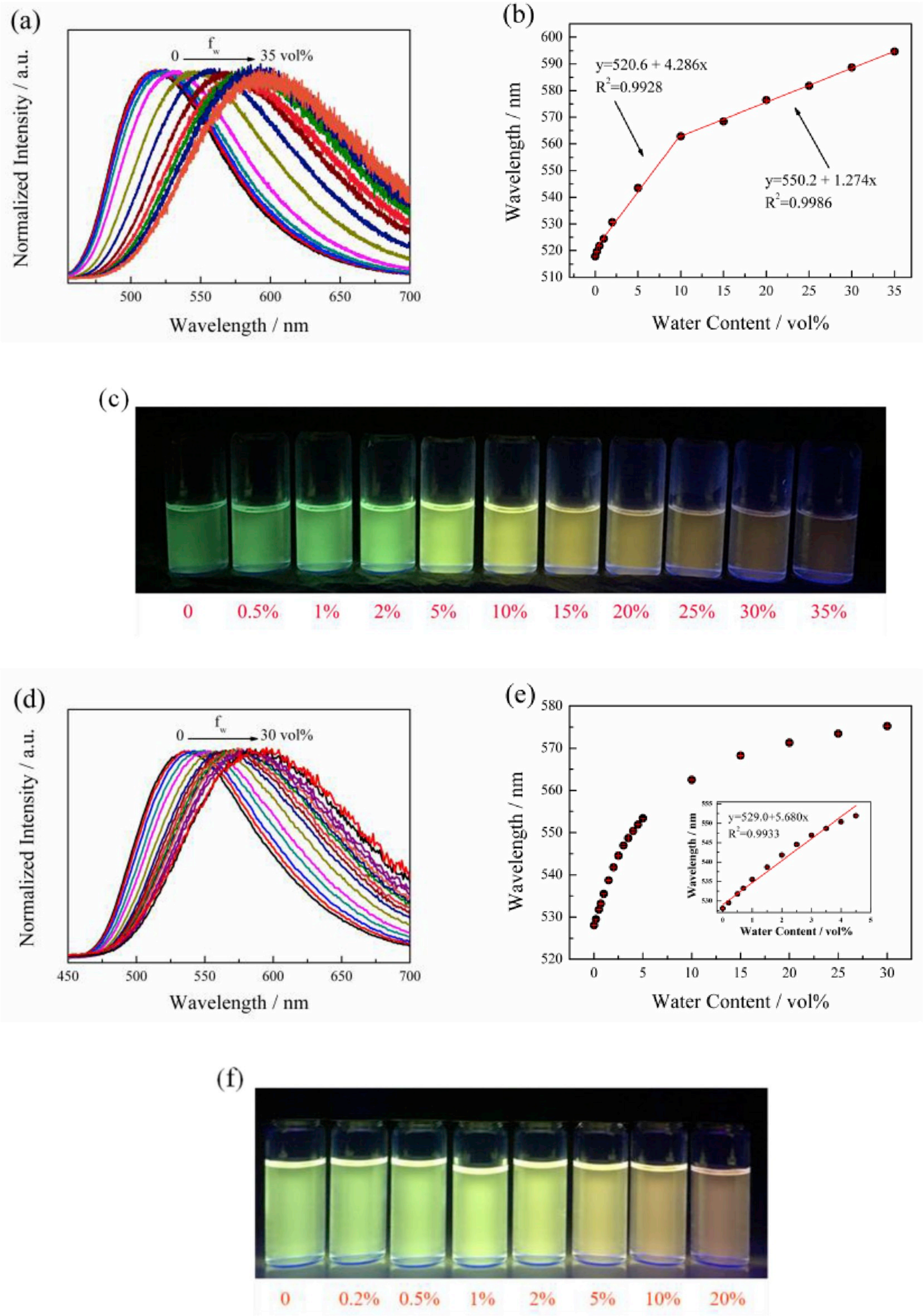


Fig. 4. Normalized fluorescence spectra and Fluorescence peak intensity of THID in (a and b) water/Diox mixture, (d and e) water/THF mixture with increasing amounts of water. Inset: photographs of THID in (c) water/Diox mixture and (f) water/THF mixture with different amounts of water taken under UV light (365 nm). Concentration: 0.5 μM; excitation wavelength: 400 nm.

[42]. The fluorescent material was found to uniformly distribute in mixed solvent without GMS, however, it could rapidly aggregate to emit green fluorescence once after introducing GMS (Fig. S14). Therefore, it could be considered that a core-shell structure should be formed in RM, in which THID aggregations could form a model like reverse micelle cladding THID aggregations (RMCAs). Furthermore, dynamic light scattering was employed to measure the RMCAs size distributions in liquid, indicated an average diameter of 709.68 nm. SEM and TEM

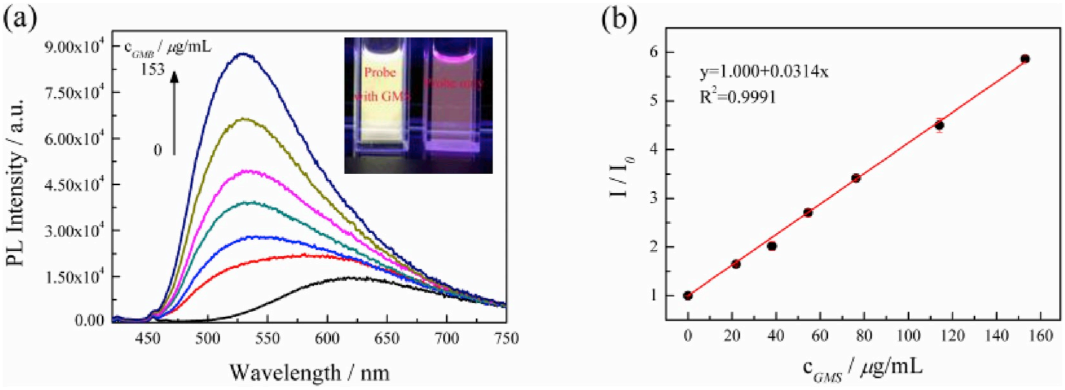


Fig. 5. (a) Fluorescence emission spectra of THID with adding different GMS concentration. Inset: photographs of THID probe solution with and without GMS (153 μg/mL) taken under UV light (365 nm). (b) Plots of the fluorescence intensity change of THID probe versus varied GMS concentration. Concentration of THID: 0.75 μM; excitation wavelength: 400 nm.

further revealed RMCAs with average diameter of ca. 123 ± 27 nm. Therefore, it was reasonable to conclude that THID molecules contacted with hydrophilic hydroxyl groups of GMS at first, then with increasing GMS concentration to exceed its CMC, THID could be taken into the hydrophilic core of GMS-RM, resulting in that THID molecules was forced to aggregate and induce aggregations emission.

To further study the selectivity of THID probe toward the GMS, various anionic, cationic, analogously nonionic surfactants as well as some common anions and cations were investigated under the identical conditions. It was found that the fluorescence of this probe could be hardly turned on by these tested surfactants and ions, suggested that the THID probe has a high selectivity for GMS (Fig. 7). Moreover, the fluorescence spectra of probe in the presence of GMS were further measured upon addition of these tested surfactants and ions, and the obtained result further supported the excellent selectivity (Fig. S15).

4. Conclusions

In this paper, the fluorescence properties of THID in thirteen solvents with different polarities have been investigated. The fluorescence color was found to be tunable from green to red by changing the solvent from nonpolar (cyclohexane) to polar (methanol), and the Stokes shifts of THID was shown to have a good linear relationship with not only the solvent polarity parameter but also the normalized molar electronic transition energy. These observations could indicate that THID molecule is strongly dependent-solvent polarity due to TICT, leading to solvatochromism. Therefore, THID could be used as a fluorescent sensor for detecting low-level water content in five water/miscible solvents, including Diox, THF, DMF, Ace and can, with low LOD. Furthermore, it was found that, in the mixed solution including GMS, THID molecule could enter into the core of RMs and form nano-aggregations. In view of “cage effect” and RIR, the configuration motion of THID was further restricted, resulting in blue-shifted emission and enhanced emission intensity with a “turn on” model. Compared with the other tested surfactants and ions THID probe could show the high selectivity for GMS.

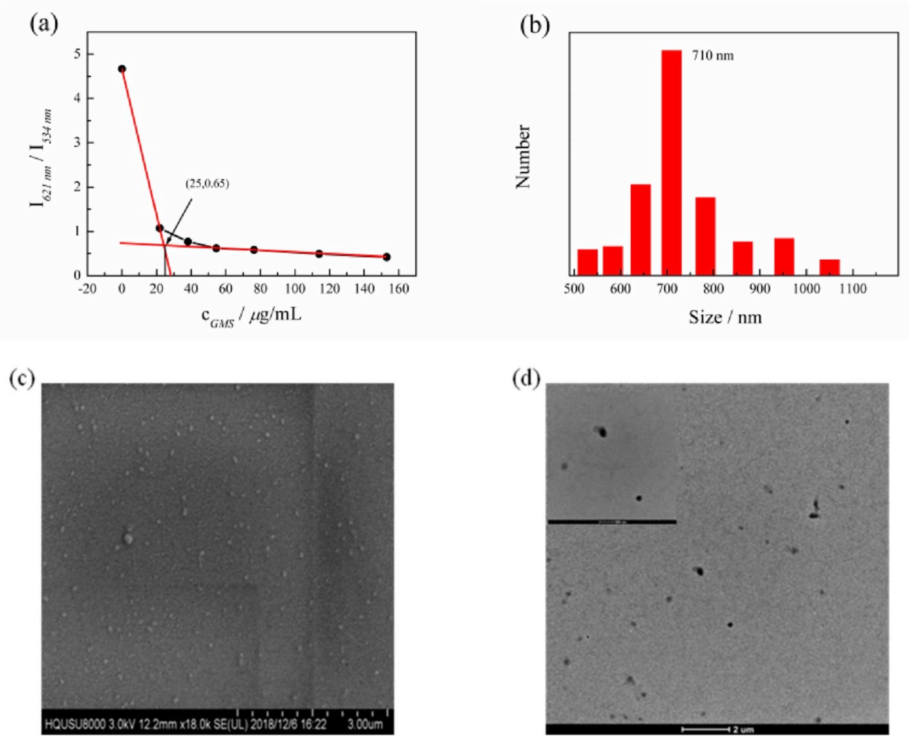


Fig. 6. (a) Plots of relative intensity ($I_{621\ nm}/I_{534\ nm}$) of THID versus the concentration of GMS in DMF/water mixture. (b) GMS-RM size by dynamic light scattering (DLS) in DMF/water mixture. (c) SEM and (d) TEM images of the GMS-RMs formed in DMF/water mixture (7:3, v/v). Concentration of THID1: 0.75 μM; Scale bar of (d) insert: 500 nm.

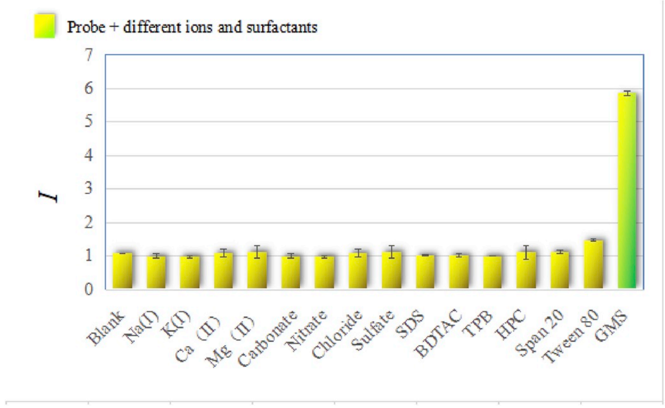


Fig. 7. Fluorescence intensity (*I*) of THID probe alone and that upon adding with different ions (0.02 M) and surfactants (concentration of surfactants were 200 μg/mL beside GMS concentration was 153 μg/mL), respectively. SDS: sodium dodecyl sulfonate; BDTAC: benzyl dimethyl tetradecyl ammonium chloride; TPB: tetradecyl pyridine bromide; HPC: hexadecyl pyridine chloride; Span 20: sorbitan monolaurate; Tween 80: polyethylene glycol sorbitan monooleate. Concentration of THID1: 0.75 μM; excitation wavelength: 400 nm.

Conflicts of interest

There are no conflicts of interest.

Acknowledgments

This study was supported by the Natural Science Foundation of China (No.21275059, 21377124 and 21575044), the Natural Science Foundation of Fujian Province (No. 2015J01054, 2016J01062 and 2014J01048) and the Foundation of Graphene Powder & Composite Research Center of Fujian Province (2017H2001). Thanks a lot for the help from Dr. Chuan-Feng Chen and his students in Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Molecular Recognition and Function for the support in THID synthesis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.talanta.2019.120214.

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